# WORLD INTELLECTUAL PROPERTY ORGANIZATION International Bureau



#### INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7:

(11) International Publication Number:

WO 00/30200

H01M 8/04, 8/06

(43) International Publication Date:

25 May 2000 (25.05.00)

(21) International Application Number:

PCT/CA99/01043

A1

(22) International Filing Date:

8 November 1999 (08.11.99)

(30) Priority Data: 09/191,049

12 November 1998 (12.11.98) US

(81) Designated States: AU, CA, DE, GB, JP, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

#### Published

With international search report.

Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(72) Inventors; and

(75) Inventors/Applicants (for US only): TILLMETZ, Werner [DE/DE]; Bayer Strasse 25, D-88131 Lindau (DE). WILKINSON, David, P. [CA/CA]; 1391 Coleman Street, North Vancouver, British Columbia V7R 1W4 (CA). COLBOW, Kevin, M. [CA/CA]; 1305 Fernwood Crescent, North Vancouver, British Columbia V7P 1K3 (CA). ST-PIERRE, Jean [CA/CA]; 2-2225 West 39th Avenue, Vancouver, British Columbia V6M 1T8 (CA).

(71) Applicant (for all designated States except US): BALLARD

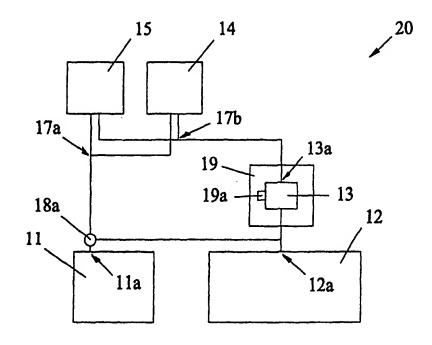
POWER SYSTEMS INC. [CA/CA]; 9000 Glenlyon Parkway, Burnaby, British Columbia V5J 5J9 (CA).

(74) Agent: DE KOCK, Elbie, R.; Russell Reyneke, Two Bentall Centre, Suite 700, 555 Burrard Street, Vancouver, British Columbia V7X 1M8 (CA).

(54) Title: FUEL CELL SYSTEM WITH IMPROVED STARTING CAPABILITY

#### (57) Abstract

method commencing operation of a fuel cell system which includes a fuel reformer is provided. During a start-up period, the same fuel (14) which is used in the feedstock to the reformer (13) is directed to at least a portion of the fuel cells (11) in the system. These fuel cells provide output power by direct oxidation of the fuel, at least until the reformer is operational, producing hydrogen-containing gas stream suitable for the fuel cells. Thus, useful output power can be obtained from the system without the delay typically associated with start-up of the reformer.



## FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
ΑT	Austria	FR	France	LU	Luxembourg	SN	Senegal
ΑÜ	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav	TM	Turkmenistan
BF	Burkina Faso	GR	Greece		Republic of Macedonia	TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Vict Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	zw	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's	NZ	New Zealand	2011	Zimodowe
CM	Cameroon		Republic of Korea	PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RÜ	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

## FUEL CELL SYSTEM WITH IMPROVED STARTING CAPABILITY

#### 5 Field Of The Invention

The present invention relates to methods and apparatus for commencing operation of a solid polymer fuel cell system. In particular, the invention relates to starting fuel cell systems that include a reformer.

10

## **Background Of The Invention**

Fuel cell systems are currently being developed for use as power supplies in numerous applications, such as transportation applications and stationary power plants. In some of these applications, the fuel cell system may operate more or less continuously for long periods, albeit at varying power levels. However, in other applications, the fuel cell system may be subjected to frequent on-off cycles and hence go through numerous starts from a shutdown condition. Automotive applications are an example of applications with such a duty cycle.

20

25

15

In general, electrochemical fuel cells convert reactants, namely fuel and oxidant fluid streams, to generate electric power and reaction products. Electrochemical fuel cells generally employ an electrolyte disposed between two electrodes, namely a cathode and an anode. An electrocatalyst is needed to induce the desired electrochemical reactions at the electrodes. In addition to electrocatalyst, the electrodes may also comprise an electrically conductive substrate upon which the electrocatalyst is deposited. Solid polymer electrolyte fuel cells employ a membrane electrode assembly ("MEA"). The MEA comprises a solid polymer electrolyte or ion-exchange membrane disposed between the two electrode layers. Solid polymer fuel cells operate at relatively low temperatures (circa 80°C) compared to other fuel cell types.

30

A broad range of reactants can be used in electrochemical fuel cells. The oxidant is typically oxygen, delivered in a substantially pure oxygen stream or in a

-2-

dilute oxygen stream such as air. The fuel is often molecular hydrogen, delivered as substantially pure hydrogen gas or in a hydrogen-containing gas stream such as a reformate stream. Other fuels, besides molecular hydrogen, may be oxidized directly at the fuel cell anode. For example, methanol, dimethyl ether, and methane may be delivered to the fuel cell anode where they are oxidized to produce protons. Such fuels may be delivered in gaseous streams. For methanol and dimethyl ether however, aqueous liquid streams are more commonly used.

5

10

15

20

25

30

A given solid polymer fuel cell can be expected to operate to some extent on most fuels, either in the gas phase or liquid phase, and therefore provide power. However, the design and operation of a solid polymer fuel cell system is typically adapted for the specific type of fuel stream (both the fuel and phase) which is to be used. Along with differences in the subsystems external to the fuel cells (e.g., fuel circulation, cooling, and/or humidification subsystems), there may also be differences in the fuel cells themselves. At this time, for instance, the anodes in direct methanol liquid feed fuel cells (i.e., cells which operate "directly" on unreformed aqueous methanol) typically employ different electrocatalysts and different electrode structures than do fuel cells supplied with hydrogen gas. Another difference between hydrogen gas and direct methanol liquid feed fuel cells might be the choice of solid polymer membrane. In direct methanol liquid feed fuel cells, there is often a problem with crossover of methanol fuel from the anode to the cathode side through the membrane. Improvements in crossover characteristics of membrane materials can be expected to lead to different membranes being preferred for each fuel cell type.

Hydrogen gas is presently a preferred fuel insofar as fuel cell operation and performance (output power) are concerned. However, it can be significantly more difficult to store and handle hydrogen than other fuels. Accordingly, in many fuel cell systems, a hydrogen-containing gaseous fuel stream is created from another fuel using a fuel processing subsystem. Typically, the fuel processing subsystem includes a reformer which generates a hydrogen-containing reformate stream from a fuel feedstock (such as methanol or natural gas), usually by reacting the fuel with

- 3 -

steam at elevated temperature in the presence of a suitable catalyst. The fuel processing subsystem also typically includes various other components to assist the reforming process, to purify the reformate stream, and/or to introduce other desirable compounds into the gas stream (e.g., vaporizer, shift converter, selective oxidizer, hydrogen separator, humidifier, etc.).

5

10

15

20

25

30

While reformer-based fuel cell systems are preferred in some applications, there are some difficulties associated with the use of reformed fuel. For instance, aside from the need for and complexity of the fuel processing subsystem itself, it can be significantly more complicated and time consuming to start up the system. Both the solid polymer fuel cells and the reformer typically operate above ambient temperature and thus generally need to be heated before normal operation can begin. The reformer in particular may need to be heated to several hundred degrees Celsius and this can take several minutes to accomplish. Further, during warm-up, operation of the reformer is usually not as efficient and any reformate produced may contain large quantities of impurities such as carbon monoxide which can poison the electrocatalysts typically employed in fuel cell anodes. Thus, any reformate produced during the start-up period may not be of much use for purposes of generating electrical power from the fuel cells. Additionally, the power output of the fuel cells themselves may be relatively low until they have reached a certain operating temperature. Finally, any water supply used in the fuel processing subsystem or in humidification of the fuel cell reactant streams is subject to freezing when ambient conditions fall below 0°C, and thus represents an additional potential difficulty for system start-up. As a result, additional subsystems may be required to provide power and/or heat just during the start-up of a reformer-based fuel cell system. For instance, fuel from the fuel feedstock supply can be burned to heat up the reformer. Once the reformer is operating, hydrogen-containing reformate is available to start up the fuel cells. Also, the reformer may be used to heat the fuel cells. This procedure however may be undesirably slow for some applications. Alternatively, a supply of substantially pure hydrogen can be maintained in the system simply for start-up purposes. The hydrogen can be

-4-

combusted (by burner or catalytic combustion) to provide heat for warming up the reformer and fuel cells. Hydrogen can also be directed to the fuel cell anodes to initiate operation of the fuel cells until a suitable supply of reformate is available. The supply of hydrogen can be stored, for example, as bottled compressed gas or absorbed in metal hydride compounds. However, the hydrogen supply must periodically be replenished. In another approach, reformer-based fuel cell systems can be started up using energy provided by storage batteries or using combinations of the preceding methods.

Direct methanol fuel cell systems (DMFCs) are not subject to the same 10 problems relating to start-up. Direct methanol fuel cells show relatively good performance during the start-up phase and thus are capable of fairly rapid start-up and can provide some useful power output when starting from ambient temperatures. Further still, methanol has a freezing point that is well below the typical lower temperature limit to which the system is exposed in most applications. Thus, methanol and certain aqueous methanol mixtures may not pose a freezing concern (although typical aqueous methanol mixtures for DMFCs are too dilute to provide significant protection against freezing). However, at this time at least, the performance and efficiency of direct methanol fuel cells is not adequate to supplant reformer-based fuel cell systems in all applications.

20

25

15

5

#### **Summary Of The Invention**

A solid polymer fuel cell system which comprises a supply of fuel and a reformer can be started up quickly by including a portion of fuel cells in the system that operates directly on a starting fluid comprising the unreformed fuel during a start-up period. Thus, within the plurality of fuel cells in the complete system, at least a first portion provides output power during the start-up period. A second portion of the fuel cells in the system, e.g., the remaining fuel cells, operate on reformed hydrogen-containing gas produced by the reformer after the start-up

- 5 -

period, and thus provide output power after a start-up period. The first portion of fuel cells are thus "starter cells" for the system.

Typically, the reformer is a part of a more complex fuel processing subsystem which includes means for producing a suitable feedstock (e.g., a mixture of fuel and steam) for the reformer. The feedstock is reformed, and may subsequently be purified and/or humidified, to create a stream of hydrogen-containing gas which is then directed to a second portion of fuel cells at normal operating temperatures. The starting fluid may also be a fuel mixture (e.g., a mixture of fuel and water) but it is not reformed. Instead a starting fluid stream comprising the fuel is directed to the first portion of fuel cells during start-up, and the fuel is oxidized directly at the starter cell anodes in the fuel cell system.

10

15

20

25

30

In principle, any fuel can be employed that is suitable for oxidation both directly (unreformed) and indirectly (after reforming). Suitable fuels may be gaseous or liquid and include for example methane, ethers such as dimethyl ether, and alcohols such as methanol. A preferred fuel however is methanol. Aside from being relatively plentiful, inexpensive, and suitable for use as a direct and indirect fuel, methanol and aqueous methanol mixtures have freezing temperatures below that of water.

It can be advantageous to adapt the "starter cells" for operation on the starting fluid stream. In that way, performance during the start-up period is enhanced. Accordingly, the construction and composition of the starter cells (in the first portion) may differ from that of the fuel cells in the second portion. For instance, if the fuel is methanol, it is advantageous to employ an anode electrocatalyst in the first portion of starter cells that is different than the anode electrocatalyst in the second portion of cells. Further, it can be advantageous to employ a membrane electrolyte in the first portion of starter cells that is different than the membrane electrolyte in the second portion of cells.

By adapting the starter cells for direct operation on the starting fluid stream, their performance will be improved on the starting fluid stream but may be worse on the hydrogen-containing gas stream. Nonetheless, after the start-up period is

- 6 -

over, it may still be advantageous to direct the hydrogen-containing gas stream to the starter cells (first portion) in order to obtain additional output power therefrom. Alternatively, the starting fluid stream may continue to be directed to the starter cells after the start-up period. In a like manner, even though the second portion of cells may not be adapted for operation on the starting fluid stream, it may still be advantageous to direct the starting fluid stream to the second portion during the start-up period in order to obtain additional output power therefrom. Thus, some or all of the fuel cells may operate initially on the starting fluid stream and then on the reformed hydrogen-containing gas stream.

5

10

15

20

25

30

The first and second portions of the plurality of solid polymer fuel cells may comprise separate fuel cell stacks (i.e., one or more stacks comprising the starter cells and one or more stacks comprising the remaining cells). On the other hand, the first portion of fuel cells may instead be interspersed among the second portion of fuel cells.

During the start-up period, the starter cells may provide enough output power to be useful in heating the reformer, in heating the second portion of fuel cells, and/or in powering a peripheral subsystem (e.g., an air compressor). Compared to starting up all the cells in the system at once, less input energy is required to start only a first portion of them. Then, the starter cells can be used as a source of energy to bootstrap and complete the start-up process.

In preferred embodiments of the method, the start-up period is typically completed when the temperature of a component in the fuel cell system reaches a pre-determined threshold value. Thus, the temperature parameter of the component may be monitored and used to trigger an end to the start-up period of the system. Since the operating temperature of the reformer is generally indicative of its ability to produce a satisfactory reformed fuel stream, its temperature may be used as the trigger in preferred embodiments. Alternatively, the temperature of the second portion of fuel cells may be used as the trigger.

In the preceding, if the characteristics of both the reformer and the fuel cells permit, preferably the starting fluid and the feedstock mixtures would be the

same, thus making it possible to store both in a common reservoir.

### **Brief Description Of The Drawings**

5

10

15

20

25

30

Figure 1a is a schematic diagram of a fuel cell system comprising a fuel supply, a fuel processing subsystem, and a fuel cell stack. Figure 1b shows the system of Figure 1a in which the fuel cell system comprises a separate "starter" stack.

Figure 2 is a schematic diagram of a first embodiment of a solid polymer fuel cell system comprising a methanol reservoir, a water reservoir, and separate fuel cell stacks adapted for operation on a methanol/water mixture and hydrogencontaining gas respectively.

Figure 3 is a schematic diagram of a second embodiment of a solid polymer fuel cell system comprising methanol, water, and starting fluid reservoirs and separate fuel cell stacks adapted for operation on a methanol/water mixture and hydrogen-containing gas respectively.

Figure 4 is a schematic diagram of a third embodiment of a solid polymer fuel cell system comprising a methanol reservoir, a starting fluid reservoir, and separate fuel cell stacks adapted for operation on a methanol/water mixture and hydrogen-containing gas respectively.

Figure 5a is a schematic diagram of a fourth embodiment of a solid polymer fuel cell system comprising a methanol reservoir, a starting fluid reservoir, and first and second groups of fuel cells in a single stack, but adapted for operation on a methanol/water mixture and hydrogen-containing gas, respectively.

Figure 5b is a schematic diagram of a fifth embodiment of a solid polymer fuel cell system similar to that of Figure 5a in which a first group of fuel cells adapted for operation on a liquid methanol/water mixture is interspersed among a second group of cells adapted for operation on hydrogen-containing gas, in a single stack.

5

10

15

20

25

30

### **Detailed Description Of The Preferred Embodiments**

A schematic diagram of a basic fuel cell system which starts on unreformed fuel and which then operates on reformed fuel is shown in Figure 1a. Unreformed fuel is first directed to fuel cell stack 1 from fuel supply 4 during a start-up period. After the start-up period, fuel is directed to fuel processing subsystem 9 comprising reformer 3, from which a hydrogen-containing gas is generated. The hydrogen-containing gas is then directed to fuel cell stack 1 instead of the unreformed fuel. Figure 1b shows a similar schematic diagram except that unreformed fuel is directed to separate starter stack 1 during the start-up period. After the start-up period, hydrogen-containing gas from the fuel processing subsystem 9 is directed to another fuel cell stack 2. Optionally, hydrogen-containing gas from the fuel processing subsystem 9 can also be directed to starter stack 1 after the start-up period is concluded. As depicted, a temperature sensor 9a monitors a temperature parameter in the fuel processing subsystem 9. When a pre-determined threshold value for the temperature parameter is reached, the temperature sensor 9a signals the conclusion of the start-up period.

A preferred fuel cell system with improved starting capability comprises a plurality of solid polymer fuel cells, a supply of methanol fuel, a starting fluid comprising a mixture of methanol fuel and water, and a fuel processing subsystem comprising a reformer. The fuel processing subsystem reforms and processes a feedstock, which also comprises a mixture of methanol fuel and water, to produce a hydrogen-containing gas stream. The starting fluid is directed to the fuel inlet of a first portion of the solid polymer fuel cells. This first portion of fuel cells is adapted for operating on the starting fluid. The feedstock is directed to the inlet of the fuel processing subsystem. The outlet of the fuel processing subsystem is fluidly connected to the fuel inlet of a second portion of the solid polymer fuel cells. The outlet of the fuel processing subsystem is however also fluidly connected to the fuel inlet of the fuel inlet of the fuel processing subsystem is however also fluidly connected to the fuel inlet of the fuel cells such that the first portion can be operated on

the starting fluid during the start-up period and on the hydrogen-containing gas stream after the start-up period. Valves may be used to switch the source of fuel stream supplied to the fuel cells.

5

10

15

20

25

30

Several different embodiments of such a methanol fueled system are shown in the following schematic Figures. (For simplicity, various conventional components, such as oxidant supply, compressors, heaters, electrical output terminals, are not shown in these Figures. Such components and their integration in an overall system are disclosed in U.S. Patent No. 5,200,278, incorporated herein by reference in its entirety.) In Figure 2, system 20 includes a first fuel cell stack 11 that is adapted for direct operation on methanol. A second fuel cell stack 12 is adapted for operation on reformate provided by reformer 13 in fuel processing subsystem 19. The system includes a methanol reservoir 14 and a water reservoir 15.

During start-up, a starting fluid stream is provided by the controlled mixing of methanol from methanol reservoir 14 and water from water reservoir 15 at junction 17a. The starting fluid is then directed through valve 18a to a fuel inlet 11a of the first fuel cell stack 11. First stack 11 generates electrical power which can be used to heat the reformer 13 or second stack 12, or to power another subsystem. Feedstock for the fuel processing subsystem 19 is provided by a controlled mixing of methanol from methanol reservoir 14 and water from water reservoir 15 at junction 17b. As the system 20 is warming up, feedstock may be directed through the reformer 13 and the fuel processing subsystem output stream may be directed through second stack 12, as is often done conventionally during a fuel system start-up period. However, typically second stack 12 would be under no electrical load during this period. An electrical load would preferably only be applied to second stack 12 once the fuel processing subsystem output stream was acceptable, and perhaps once second stack 12 reached a desirable operating temperature.

When reformer 13 is at a suitable operating temperature as indicated by temperature monitor 19a, feedstock is then directed to reformer inlet 13a. The

5

10

15

20

25

30

hydrogen-containing gas output of fuel processing subsystem 19 is then directed to the inlet 12a of the second stack 12. At this point, it may be desirable to stop the flow of starting fluid to first stack 11 and, instead, to direct the hydrogen-containing gas to inlet 11a via valve 18a. Output power may then be obtained from both first and second stacks 11, 12 operating on hydrogen-containing gas from the fuel processing subsystem 19 after start-up.

In part due to methanol crossover issues, conventional direct methanol fuel cells typically operate on methanol/water solutions that have methanol concentrations in the range of from about 1 to 13% by weight. Thus, the starting fluid prepared at junction 17a may have methanol concentrations in that range. The reformer 13 however typically operates on feedstocks with methanol weight concentrations of about 60%. (Stoichiometrically, one mole of methanol is reacted with one mole of water in the reforming reaction. However, an excess of water is typically employed in practice.)

The methanol concentrations in the starting fluid and feedstock provide some protection against freezing (with freezing points of order of -10°C and -80°C respectively) in certain areas of the system 20. It may also be possible to use an additive (e.g., ethylene glycol) in the water reservoir 15 to protect it from freezing. However, any additive would have to be compatible with both the fuel cells in first stack 11 and the reformer 13. Also, any additive present should not lead to the production of a hydrogen-containing gas stream which would be incompatible for use in second stack 12. Methanol, of course, is a suitable additive and using an appropriate amount effectively provides a reservoir of starting fluid as shown in the following alternative embodiments.

Figure 3 shows another embodiment of a fuel cell system 30 which also includes first and second fuel cell stacks 21, 22, a fuel processing subsystem 29 comprising a reformer 23, and a methanol reservoir 24, each of which is similar in construction and operation to those shown in Figure 2. However, a starting fluid reservoir 26 comprising a supply of starting fluid is included and a different procedure may be followed with regards to water reservoir 25.

- 11 -

In Figure 3, during start-up, a starting fluid is provided directly from starting fluid reservoir 26 through valve 28a to fuel inlet 21a of the first fuel cell stack 21. Feedstock for the reformer is provided by the controlled mixing of methanol from methanol reservoir 24 and water from water reservoir 25 at junction 27b. Again, the feedstock is directed to reformer inlet 23a. Here, a supply of water for the water reservoir 25 is obtained from the product water generated by the operating first and/or second fuel cell stacks 21, 22. Thus, water from first stack outlet 21b and second stack outlet 22b is collected and directed into water reservoir 25. At system shutdown, the water reservoir 25 may be emptied so as to avoid freezing. In this embodiment, it may be possible to rely on the production of water from the first stack 21 during start-up to prepare a sufficient amount of aqueous feedstock for the reformer, after which production of water is used from both stacks 21, 22 after start-up.

5

10

15

20

25

Figure 4 shows still another embodiment of a fuel system 40. As in Figure 3, system 40 includes first and second fuel cell stacks 31, 32, a fuel processing subsystem 39 comprising a reformer 33, a methanol reservoir 34, and a starting fluid reservoir 36, each of which is similar in construction and operation to those shown in Figure 3. The water reservoir has been omitted.

In Figure 4, during start-up, a starting fluid is again provided directly from starting fluid reservoir 36 through valve 38a to fuel inlet 31a of the first fuel cell stack 31. Feedstock for the reformer may be provided by the controlled mixing of methanol from methanol reservoir 34 and the starting fluid mixture from starting fluid reservoir 36 at junction 37b. This embodiment is viable in principle as long as the desired concentration of methanol in the feedstock is higher than that in the starting fluid. Starting fluid may be obtained by mixing product water generated by the operating first and/or second fuel cell stacks 31, 32 (coming from first and second stack outlets 31b and 32b respectively) and methanol from methanol reservoir 34. While the embodiment in Figure 4 requires one less reservoir than that in Figure 3, the former requires additional material balancing considerations in

that the proportions of methanol and water fed to starting fluid reservoir 36 have to be carefully controlled, and be uniformly mixed in the reservoir 36.

5

10

15

20

25

30

A still further embodiment of a fuel cell system 50 is shown in Figure 5a, which is similar to that of Figure 4 except that now, an entire fuel cell array 41 is supplied with starting fluid from starting fluid reservoir 46 during start-up through valve 48a to fuel inlet 41a. After start-up, valve 48a is switched to supply hydrogen-containing gas from reformer 43 to fuel inlet 41a instead. As shown in Figure 4, certain fuel cells in the fuel cell stack, namely, first portion 41y, are adapted for operation on the unreformed starting fluid and the remainder, second portion 41z, are adapted for operation on hydrogen-containing gas. Figure 5a shows an arrangement where first portion 41y is adjacent to second portion 41z. Figure 5b shows a similar embodiment except that the fuel cells in first portion 41y are interspersed among the fuel cells in the second portion 41z in stack 41. Note however that it may not be desirable for any fuel cells to be adapted for operation on starting fluid in these embodiments because the output power from the entire array operating on the starting fluid may be sufficient for start-up purposes without any special modification of any fuel cells. An advantage of these embodiments generally is that separate manifolding and electrical connections to each fuel cell portion are not required. Another advantage is that the integration of the fuel cell portions in a single stack promotes efficient heat transfer during the warm-up period (particularly in the embodiment shown in Figure 6). However, all the cells in the fuel cell stack must undergo a transition between fuel supplies at the end of the start-up period in these embodiments.

If starting fluid mixtures of high enough methanol concentration can be used successfully, the composition of the starting fluid mixture and the feedstock mixture can be made the same. In that case, a further simplification of the above apparatus is possible in principle (e.g., 0 reservoir 34 could be used).

While particular elements, embodiments and applications of the present invention have been shown and described, it will be understood, of course, that the invention is not limited thereto since modifications may be made by those skilled in

- 13 -

the art without departing from the spirit and scope of the present disclosure, particularly in light of the foregoing teachings.

#### What is claimed is:

10

15

1. A method of commencing operation of a fuel cell system, said system comprising a plurality of solid polymer fuel cells, a supply of fuel, and a fuel processing subsystem comprising a reformer which processes a feedstock comprising said fuel to produce a hydrogen-containing gas stream, said method comprising:

directing a starting fluid stream comprising said fuel to at least a first portion of said plurality of solid polymer fuel cells during a start-up period, whereby said first portion provides output power during said start-up period; and

directing said hydrogen-containing gas stream from said fuel processing subsystem to at least a second portion of said plurality of solid polymer fuel cells after said start-up period, whereby said second portion provides output power after said start-up period.

- 2. The method of claim 1 wherein said first portion of said plurality of solid polymer fuel cells is adapted for operation on said starting fluid stream.
- 3. The method of claim 2 wherein said first portion of said plurality of solid polymer fuel cells comprises an anode electrocatalyst that is different than the anode electrocatalyst of said second portion of solid polymer fuel cells.
- The method of claim 2 wherein said first portion of said plurality of solid
   polymer fuel cells comprises a membrane electrolyte that is different than the
   membrane electrolyte of said second portion of solid polymer fuel cells.
  - 5. The method of claim 1 further comprising directing said hydrogencontaining gas stream to said first portion of said plurality of solid polymer fuel

cells after said start-up period, whereby said first portion provides output power after said start-up period.

- 6. The method of claim 2 further comprising directing said starting fluid stream to said first portion of said plurality of solid polymer fuel cells after said start-up period whereby said first portion provides output power after said start-up period.
- 7. The method of claim 1 further comprising directing said starting fluid stream to said second portion of said plurality of solid polymer fuel cells during said start-up period, and directing said hydrogen-containing gas stream to said first portion of said plurality of solid polymer fuel cells after said start-up period.
- 8. The method of claim 6 wherein said first portion of said plurality of solid polymer fuel cells is interspersed among said second portion of said plurality of solid polymer fuel cells.
- The method of claim 6 wherein said first portion of said plurality of solid polymer fuel cells and said second portion of said plurality of solid polymer fuel
   cells are located in separate fuel cell stacks in said fuel cell system.
  - 10. The method of claim 1 wherein said fuel is a liquid.
- 11. The method of claim 10 wherein the freezing point of said starting fluidstream is lower than that of water.
  - 12. The method of claim 10 wherein said fuel comprises methanol.
- 13. The method of claim 12 wherein said starting fluid stream comprises a30 mixture of methanol and water.

- 14. The method of claim 1 wherein said fuel comprises dimethyl ether.
- 15. The method of claim 1 further comprising heating said reformer using said
  output power of said first portion of said plurality of solid polymer fuel cells during said start-up period.
  - 16. The method of claim 1 further comprising heating said second portion of said plurality of solid polymer fuel cells using said output power of said first portion of said plurality of solid polymer fuel cells during said start-up period.
  - 17. The method of claim 1 further comprising powering a peripheral subsystem using said output power of said first portion of said plurality of solid polymer fuel cells during said start-up period.

15

10

- 18. The method of claim 1 further comprising monitoring a temperature parameter in said fuel cell system and concluding said start-up period when said temperature parameter reaches a pre-determined threshold value.
- 20 19. The method of claim 18 wherein said temperature parameter is the operating temperature of said reformer in said fuel processing subsystem.
  - 20. The method of claim 18 wherein said temperature parameter is the temperature of said second portion of said plurality of solid polymer fuel cells.

25

21. The method of claim 13 further comprising:

providing a methanol reservoir in said fuel cell system;
providing a water reservoir in said fuel cell system;
using methanol from said methanol reservoir and water from said
water reservoir in said starting fluid stream; and

30

using methanol from said methanol reservoir and water from said water reservoir in said feedstock for said reformer.

### 22. The method of claim 13 further comprising:

providing a methanol reservoir in said fuel cell system;

providing a water reservoir in said fuel cell system;

directing product water from said plurality of solid polymer fuel cells to said water reservoir;

providing a starting fluid reservoir in said fuel cell system;
using said starting fluid reservoir to store said starting fluid; and
using methanol from said methanol reservoir and water from said
water reservoir in said feedstock for said reformer.

### 23. The method of claim 13 further comprising:

10

15

20

providing a methanol reservoir in said fuel cell system;

providing a starting fluid reservoir in said fuel cell system;

directing methanol from said methanol reservoir and directing

product water from said plurality of solid polymer fuel cells to said starting

fluid reservoir;

directing said starting fluid from said starting fluid reservoir to said first portion of said plurality of solid polymer fuel cells; and using methanol from said methanol reservoir and said starting fluid from said starting fluid reservoir in said feedstock for said reformer.

25 24. The method of claim 23 wherein the method further comprises: directing said starting fluid stream to said plurality of solid polymer fuel

cells during said start-up period, whereby said plurality of solid polymer fuel cells provides output power during said start-up period; and

PCT/CA99/01043 WO 00/30200

- 18 -

directing said hydrogen-containing gas stream to said plurality of solid polymer fuel cells after said start-up period, whereby said plurality of solid polymer fuel cells provides output power after said start-up.

- 25. The method of claim 24 wherein said first portion of said plurality of solid 5 polymer fuel cells are adapted for operating on said starting fluid stream.
  - 26. The method of claim 25 wherein said first portion of said plurality of solid polymer fuel cells is interspersed among said second portion of said plurality of solid polymer fuel cells.
    - 27. The method of claim 13 wherein said starting fluid for said starting fluid stream and said feedstock for said reformer are the same and are stored in a common fuel reservoir.

15

20

25

30

10

- 28. A fuel cell system with improved starting capability comprising:
  - a plurality of solid polymer fuel cells;
  - a supply of fuel; and
  - a fuel processing subsystem comprising a reformer for processing a feedstock comprising said fuel to produce a hydrogen-containing gas stream, said fuel processing subsystem fluidly connected to receive fuel from said fuel supply;

wherein at least a first portion of said plurality of solid polymer fuel cells is fluidly connected to receive said fuel from said fuel supply, and at least a second portion of said plurality of solid polymer fuel cells is fluidly connected to receive said hydrogen-containing gas stream from said fuel processing subsystem.

29. The fuel cell system of claim 28 wherein said first portion of said plurality of solid polymer fuel cells is adapted for operating on a starting fluid comprising said fuel.

- 19 -

30. The fuel cell system of claim 29 wherein said first portion of said plurality of solid polymer fuel cells comprises an anode electrocatalyst that is different than the anode electrocatalyst of said second portion of solid polymer fuel cells.

5

- 31. The fuel cell system of claim 29 wherein said first portion of said plurality of solid polymer fuel cells comprises a membrane electrolyte that is different than the membrane electrolyte of said second portion of solid polymer fuel cells.
- 32. The fuel cell system of claim 29 wherein said first portion of said plurality of solid polymer fuel cells is interchangeably fluidly connected to receive said hydrogen-containing gas from said fuel processing subsystem.
  - 33. The fuel cell system of claim 28 wherein said fuel comprises methanol.

15

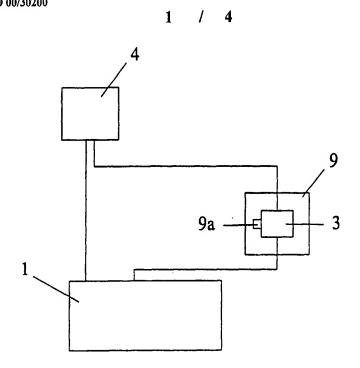


FIG. 1a

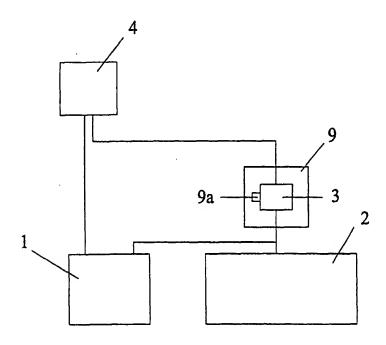


FIG. 1b

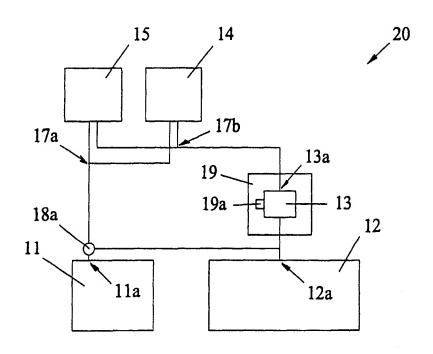
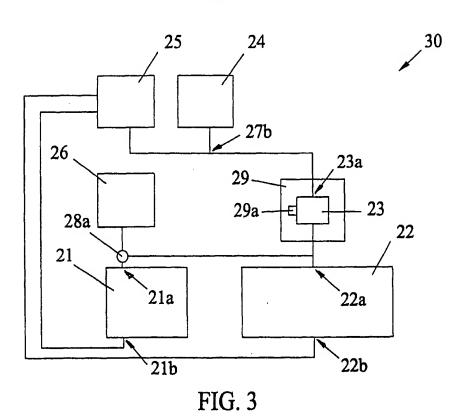


FIG. 2



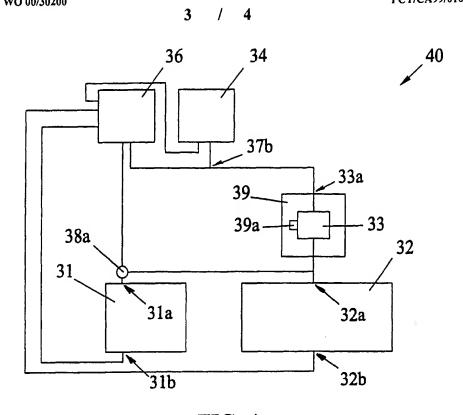


FIG. 4

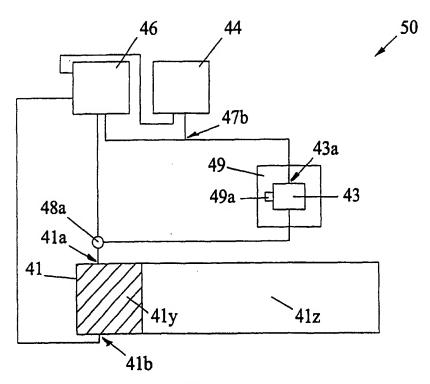


FIG. 5a

4 / 4

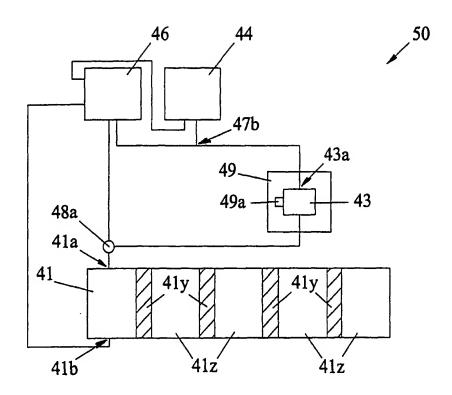


FIG. 5b

## INTERNATIONAL SEARCH REPORT

Inten mai Application No PCT/CA 99/01043

A. CLASSI IPC 7	FIGATION OF SUBJECT MATTER H01M8/04 H01M8/06				
According to	o International Patent Classification (IPC) or to both national class	ification and IPC			
	SEARCHED				
	ocumentation searched (classification system followed by classific	cation symbols)			
IPC 7	H01M				
Documenta	tion searched other than minimum documentation to the extent th	at such documents are included in the fields a	earched		
Electronic d	lata base consulted during the international search (name of data	base and, where practical, search terms use	d)		
C. DOCUM	ENTS CONSIDERED TO BE RELEVANT				
Category *	Citation of document, with indication, where appropriate, of the	relevant passages	Relevant to claim No.		
A	US 5 482 790 A (YAMADA SHUJI E 9 January 1996 (1996-01-09)	T AL)			
Α	EP 0 729 196 A (FINMECCANICA SP 28 August 1996 (1996-08-28)				
A	WO 94 02409 A (CDSS LTD ;FOX TH (GB)) 3 February 1994 (1994-02-				
Α	AMPHLETT J C ET AL: "SOME DESI CONSIDERATIONS FOR A CATALYTIC STEAM REFORMER FOR A PEM FUEL C GENERATING SYSTEM" PROCEEDINGS OF THE INTERSOCIETY CONVERSION ENGINEERING CONFEREN YORK, IEEE, vol. CONF. 26, 1991, pages 642-XP000299778 ISBN: 0-89448-163-0	METHANOL ELL POWER ENERGY ICE,US,NEW			
Furt	her documents are listed in the continuation of box C.	X Patent family members are listed	l in annex.		
	ategories of cited documents :	T' later document published after the into	emational filing date		
	ent defining the general state of the art which is not dered to be of particular relevance	or priority date and not in conflict with cited to understand the principle or th invention			
"E" earlier	document but published on or after the international	"X" document of particular relevance; the			
"L" docume	ent which may throw doubts on priority claim(s) or	cannot be considered novel or canno involve an inventive step when the do	ocument is taken alone		
citatio	is cited to establish the publication date of another in or other special reason (as specified)	"Y" document of particular relevance; the cannot be considered to involve an ir	ventive step when the		
	ent referring to an oral disclosure, use, exhibition or means	document is combined with one or m ments, such combination being obvio			
	ent published prior to the international filing date but han the priority date daimed	in the art.  *&* document member of the same patent family			
Date of the	actual completion of the international search	Date of mailing of the international se	erch report		
2	May 2000	10/05/2000			
Name and	mailing address of the ISA	Authorized officer			
	European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijawijk				
	Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	D'hondt, J	D'hondt, J		

# INTERNATIONAL SEARCH REPORT

Information on patent family members

inter nel Application No PCT/CA 99/01043

Patent document cited in search report		. Publication date	Patent family member(s)		Publication date
US 5482790	A	09-01-1996	JP DE DE US	6140065 A 4329323 A 4345319 C 5434015 A	20-05-1994 10-03-1994 03-07-1997 18-07-1995
EP 0729196	Α	28-08-1996	JP	8287936 A	01-11-1996
WO 9402409	Α	03-02-1994	AU	4580193 A	14-02-1994

Form PCT/ISA/210 (patent family annex) (July 1992)